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A NON-CYANIDE BRASS PLATING BATH

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Brass electrodeposits are used for decorative applications and for promotion of adhesion of rubber to steel and other metals. Brass coatings, because of their lubricity, are applied on rods and wires which are further subjected to drawing into thinner gauge. Brass deposits are generally obtained from cyanide electrolytes. With a view to exploring the usefulness of a noncyanide formulation, solutions with nitrilo-triacetate complexes were experimented upon for brass deposition. Studies were undertaken to identify a suitable non-cyanide brass plating bath. The results of experiments on cathodic efficiency, rate of build up and the percentage composition of the alloy deposits from the bath so identified are reported in this paper.

Keywords: Brass plating, non-cyanide and nitrilotriacetic acid

INTRODUCTION

As early as 1841 [1] the electrodeposition of brass was discovered. The chief applications of brass deposition are for decorative purposes, protection of steel, promotion of rubber adhesion to steel and other metals. Brass as an undercoat was given for nickel on aluminium substrate. Brass coatings because of their lubricity are applied on rods so that these rods can be drawn into wires [2]. From a cyanide bath the deposition potentials for copper, zinc and brass were measured in 1887 [3]. The deposition potentials of copper and zinc are sufficiently so close together in the cyanide plating solution that variations in the concentrations of some of its constituents can interchange the relative mobilities of the two metals. The percentage of copper in the brass deposit depends mainly on its concentration in the bath [4].

The problem of disposal of cyanide waste and the decomposition of the bath during operation which necessitates frequent addition of cyanide are the major problems in cyanide baths. Efforts were made to deposit brass from thiocyanates [5], sulphates [6], oxalates [7], triethanolamine [8], glycerol [9], thiosulphates [10] tartarates [11] and pyrophosphates [12]. However non noncyanide bath has come to be commercially operated, probably because each bath has some disadvantage compared to the cyanide brass plating. For example the deposits from the noncyanide bath may not be of right colour or cannot be deposited directly on steel due to the formation of an immersion deposit. Immersion deposits should be avoided and efforts were made to develop a substitute for cyanide bath to give better current efficiency and throwing power. Since nitrilotriacetic acid (NTA) does not form immersion deposits of copper, detailed investigations have been undertaken to develop a bath composition based on NTA for alloy deposition.

EXPERIMENTAL

Cold rolled steel plates (10 x 7.5 x 0.05 cm) were electrocleaned anodically for 3 minutes in a solution of 35 gpl NaOH, 25 gpl Na_2CO_3 at 343 K. They were washed in running water and this followed by a dip for 10 seconds in 5% (v/v) H_2SO_4 solutions. Finally through washing were resorted to followed by a distilled water dip.

Hull cell studies

Hull Cell experiments were then carried out with solutions containing varying quantities of $CuSO_4$ and $ZnSO_4$ in order to optimize the conditions for production of good deposits. A cell current of 1 A was used for a duration of 10 minutes. A regulated power supply was used as the d.c. source and a calibrated ammeter along with the cell constituted the electrical circuit. Soluble anodes were used.

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Current efficiency studies

Brass deposits of different compositions were obtained by varying cell and solution parameters. The current efficiency and the rate of build up were calculated as

$$\text{Percentage of current efficiency} = \frac{M \times 100}{e_{brass} \times Q}$$

where M is the mass of the alloy deposit, e_{brass} is the electrochemical equivalent of brass and Q is the quantity of electricity passed (A/sec).

Removal and analysis of the deposit

Initially attempts were made to deposit brass on stainless steel so that it could be easily pealed off for analysis. As the deposit was found to be powdery and non-uniform on stainless steel, nickel plated mild steel was employed as the basis for brass deposit got pealed off along with brass interfering with the analysis. Various substrates like inclined mild steel, anodically passivated mild steel were tried in vain. Finally brass could be electrodeposited on copper and removed chemically by immersion in 1:2 HNO_3, and the resulting solution containing copper and zinc was analysed. Extensive care has been taken in the analysis of zinc and the amount of copper in the deposit was calculated from the difference in mass of the deposit and that of the zinc determined. Zinc content in solution was analysed both by volumetric and by atomic absorption spectrophotometry.

A modified procedure for analysis of zinc from the conventional one [13] was employed. The zinc content of each deposit was estimated by precipitating out copper as cuprous thiocyanate. The filtrate was titrated against EDTA for zinc present in it using Eriochorme black T as the indicator (*p*H of 10 adjusted with NH_3 and NH_4Cl). A change in colour of the solution from pink to blue was taken as the end point.

Microhardness

The microhardness of the brass electrodeposit was determined by using PMT-3 Microscope Hardness meter (USSR Model) on the Vicker's scale. This uses diamond pyramid of a square base with an angle of 136° at the vertex between two opposite faces. The microhardness of the deposit in kg/mm^2 was determined in each case by using the following formula

$$\text{Hardness} \left(\frac{kg}{mm^2}\right) = \frac{1854 \times P}{d^2}$$

where P is the load applied in grams and d is diagonal of the indentation (μm).

Porosity

The brass electrodeposits were degreased, electrocleaned and dried. The ferroxyl solution was prepared by dissolving NaCl and white gelating in distilled water at 45°C to obtain a concentration of 0.86 *M* NaCl. Filter paper strips of 25 x 25 mm size each were impregnated with the above solution and dried. Before placing a strip on the plated surface it was moistened with a few drops of NaCl solution.After 3 minutes the papers were removed and placed at once in a $K_3Fe(CN)_6$ solution. The porosity of each deposit was evaluated on the basis of the number of blue spots formed.

RESULTS

NTA bath development studies — Hull cell studies

Depending on the solution composition either copper rich or zinc or zinc rich deposits could be obtained. Table I presents the optimised three compositions for the successful deposition of brass. The effects of temperature and stirring on bath composition 'A' revealed interesting features [Fig. 1 patterns 1-4]. Increase of temperature favoured baser metal deposition as in the case of conventional cyanide baths. The preferential deposition of nobler metals could be obtained only when the solution was stirred.

Current efficiency studies

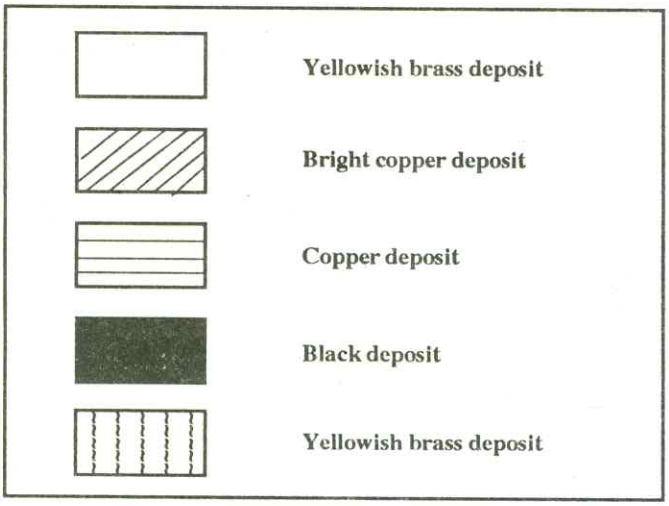
Table II presents the current efficiencies and rate of build-up at different c.d. in various baths.Current efficiency decreased while rate of build-up increased with increase in c.d in all the baths studied. For a given c.d., increase of copper contents has no effect on the current efficiency in the range studied. Increase of $ZnSO_4$ concentration increased the current efficiency at a given c.d. 99.9% efficiency of deposition was observed from bath 'C' at 0.3 A/dm^2.

Alloy composition studies

Increase of zinc concentration in the bath increased the zinc content in the deposit in the c.d. range studied [Fig. 2]. A

TABLE I: Typical bath compositions used for brass deposition

Bath	Composition		
A	NaOH	30.000 gpl	(0.750 *M*)
	NTA	47.800 gpl	(0.250 *M*)
	$ZnSO_4$	12.000 gpl	(0.042 *M*)
	$CuSO_4$	12.000 gpl	(0.048 *M*)
	*p*H	10.500	
B	NaOH	0.750 *M*	(30.000 gpl)
	NTA	0.250 *M*	(47.800 gpl)
	$ZnSO_4$	0.042 *M*	(12.000 gpl)
	$CuSO_4$	0.088 *M*	(22.000 gpl)
	*p*H	10.500	
C	NaOH	0.750 *M*	(30.000 gpl)
	NTA	0.250 *M*	(47.800 gpl)
	$ZnSO_4$	0.077 *M*	(22.000 gpl)
	$CuSO_4$	0.048 *M*	(12.000 gpl)
	*p*H	10.500	



Legends used for hull cell plating

linear relationship was obtained between the percentage of zinc in the solution and in the deposit with a slope of 1.1 ± 0.1 at all current densities. At constant $ZnSO_4$ concentration, increase of copper in the solution resulted in the increase of copper in the deposit (Fig. 3). There was a steep increase in the concentration of copper in the deposit of upto 46% of copper in the solution at all c.d. and further increase of copper in the solution had only a marginal effect.

Studies on the alloy electrodeposits

Physicochemical tests

Increase of current density had no influence on the hardness of the deposit obtained from bath 'A' while the hardness increased when deposited from bath 'B'. In bath 'C' the current density of the electrodeposition varied the hardness of the deposit. A harder deposit of 212.5 kg/mm^2 was obtained only from bath 'A'.

All the baths produced deep yellow, deep pinkish yellow and pale yellow deposits. Whitish yellow deposit was obtained at 0.7 A/mm from bath 'C' (Table III). Table IV presents the porosity of the deposits from different baths. Thickness of

TABLE II: Current efficiency and rate of build up at different current densities and at 303 K

No.	Bath	Current density (A/dm^2)	Current efficiency (%)	Rate of build up (μm/hr)
1.	A	0.3	94.1	4.2
		0.4	92.2	5.5
		0.5	90.2	6.7
		0.6	88.5	8.6
		0.7	86.3	9.0
2.	B	0.3	94.0	4.2
		0.4	92.0	5.5
		0.5	90.0	6.7
		0.6	89.0	8.6
		0.7	86.0	9.0
3.	C	0.3	99.9	4.9
		0.4	99.8	6.3
		0.5	98.3	7.8
		0.6	95.6	9.1
		0.7	85.3	9.5

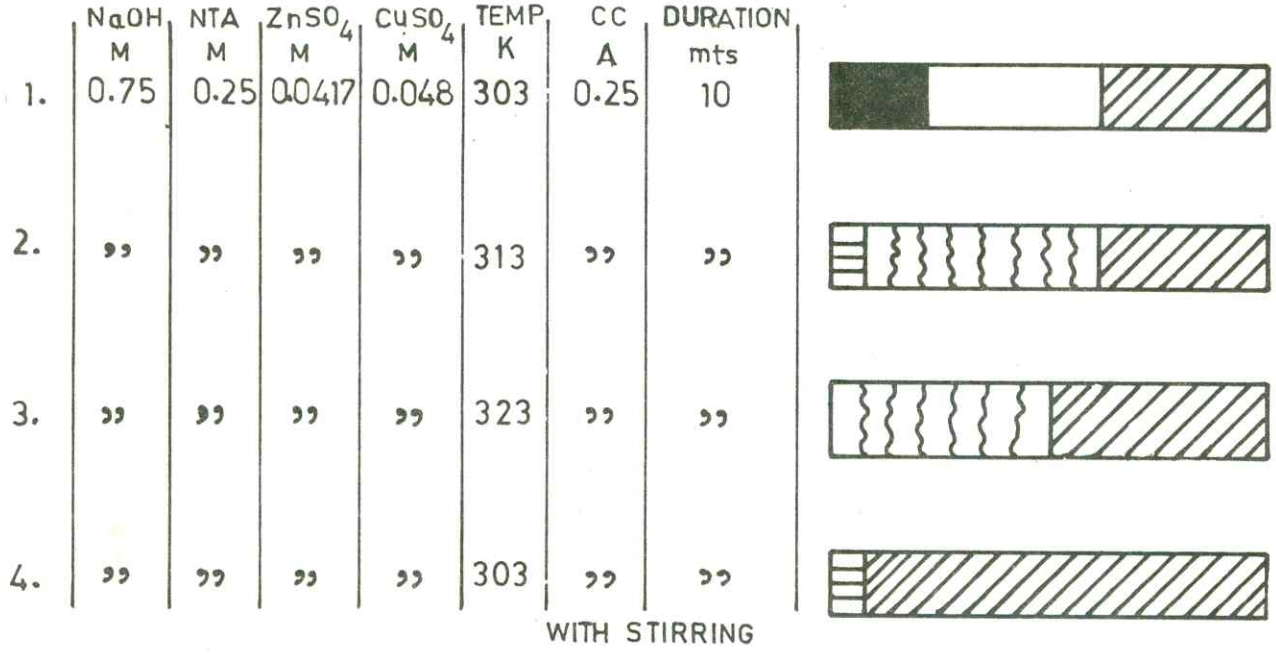


Fig. 1: Effect of temperature and stirring on bath composition 'A' in the production of brass deposit

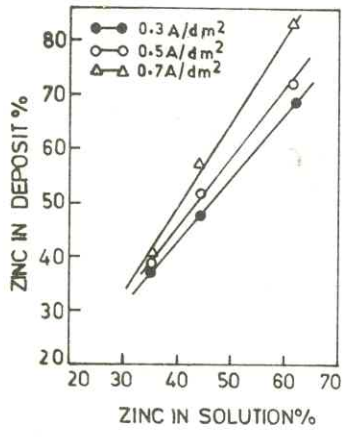


Fig. 2: Effect of zinc content in the deposit in relation to zinc concentration in solution

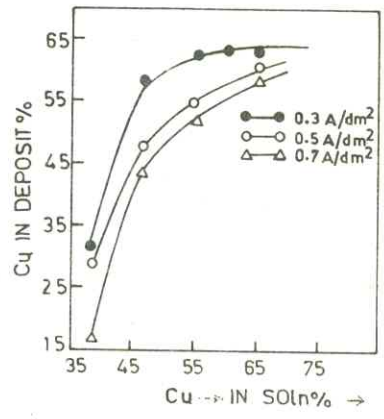


Fig. 3: Relationship between the percentage of copper in the deposit and in the solution

around 2.5 μM produced very low porous coatings. Pore free coatings were observed above 2.5 μM thickness.

CONCLUSIONS

A search of non-cyanide plating bath for brass on steel resulted in the development of Nitrilotriacetic acid based plating baths for brass. The bath can be operated with 99% efficiencies at low current densities and compositions of zinc and copper can be varied. The electrodeposits of 2.5 μM thickness were pore free and have the hardness of 212.5 kg/mm^2.

TABLE III: Properties of the brass deposits obtained at different current densities and at 303 K

Bath	Current density (A/dm^2)	Hardness (kg/mm^2)	Nature of the deposit
A	0.3		
	0.4		Deep yellow
	0.5	212.5	
	0.6		
	0.7		
B	0.3	140.0	
	0.4	174.0	Deep pinkish
	0.5	174.0	yellow
	0.6	181.0	
	0.7	203.0	
C	0.3	136.0	Pale yellow
	0.4	195.0	
	0.5	—	
	0.6	151.0	
	0.7	188.0	Whitish yellow

TABLE IV: Porosity of brass deposits of different thickness obtained at 0.5 A/dm^2 at 303 K

Bath	0.5	1.0	1.5	2.0	2.5	3.0	6.0
A	3 psc	2 psc	1 psc	1 psc	NP	NP	NP
B	1/2 ap	1/3 ap	3 psc	2 psc	NP	NP	NP
C	1/3 ap	3 psc	2 psc	1 psc	NP	NP	NP

The diameter of each pore is approximately 1 mm
psc = pores per sq.cm, ap = area porous and NP = no pore

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